# FABRICATION OF ROBUST WETTABILITY GRADIENTS ON SOFT SURFACES THROUGH PHYSICOCHEMICAL MODULATIONS

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*as partial requirement for the award of the Degree of*

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**IN**

**CHEMISTRY**

by

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## ABSTRACT

Physicochemical characteristics of the surfaces play important roles in the properties and functionalities of soft materials. Adhesion, adsorption and wettability properties of the surfaces determine the nature of interfacial interactions of soft materials with their surroundings. Leveraging this, spatially modulated interfacial phenomena can be achieved using morphological and chemical gradients on soft surfaces. In this thesis, we describe our studies on the development of new methodologies for the preparation of softness gradients and the applications of the gradients thus prepared. We developed generic and simple spin coating-based method for the fabrication of morphological gradients on soft substrates, polydimethylsiloxane (PDMS) making use of buckling instability in a homogenous bilayer system with different elasticities in each layer. Uniform wrinkles were formed through uniform thermal curing and hierarchical wrinkles through differential thermal curing of the bilayer system. The prepared wrinkles exhibit tunability in wrinkling parameters, mechanoresponsive optical properties, enhanced fog collection and triboelectric charge generation. We developed a new strategy - differential thermal curing, based on thermally modulated crosslinking of the elastomer (PDMS) for the preparation of wettability gradients on its surface. Also, we have identified and applied a strategy based on selective chemical inhibition of curing of partial cured PDMS for the wettability gradients prepared on the surface. Cell adhesion studies and directional water collection from fog using the prepared wettability gradients were also studied. Optical profilometry, optical microscopy and contact angle measurements were used for the characterization of the gradients prepared. Nebulization of droplets and condensation of water vapor were also analyzed on the surface. The thesis is designed in such a way that each chapter (except for the introduction and conclusions chapter) is describing the studies leading to the development of the strategy for gradient fabrication and the applications of gradients prepared through the new method.



***Keywords:*** Soft surface wrinkles, Morphological gradients, PDMS, Wettability, Surface patterns, Buckling instability.

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## 1. Introduction

Gradients on surfaces are composed of chemical or physical properties that gradually vary over distance. During the past half century, researchers from various disciplines of materials chemistry have been attracted towards the fabrication of gradient soft surfaces. Gradients are observed ubiquitously in nature like in carnivorous plants e.g. Venus fly trapper[1]–[3]. Based on the method of preparation gradients can generally be divided into two groups: (i) direct deposition, and (ii) post-deposition modification methods. In the first one, gradients are developed on a parent substrate by unevenly depositing the materials through natural or artificial methods. In the post-deposition methods, desorption or controlled removal of coated materials from a parent material is used to create the gradients[4]. Gradient surfaces can be classified on the basis of dimensionality, time dependency, length scale, composition, functionality, and directionality. Gradients of various types exhibit different physicochemical nature and functionalities. Another classification of gradients are as physical and chemical gradients. Chemical gradients or wettability gradients on soft surfaces can be prepared by increasing or decreasing the concentration of a surface bound species gradually across the surface. Morphological gradients (physical gradients) are obtained by altering specific morphological features across the soft surfaces in incremental or decremental fashion. Chemical and morphological gradients on soft surfaces find applications in a variety of areas such as microfluidics, droplet movement, cell adhesion, enzyme adsorption, and polymerization[2]. Investigations for technically simple and inexpensive methods for the preparation of gradients on soft matter surfaces is thus an active research area in materials science[5].

Several research groups had investigated the possibilities of preparing gradients on soft surfaces. A pioneering work was published by Chaudhury and Whitesides, using vapor diffusion and distance-dependent exposure of a polished Si wafer to vapors of decyltrichlorosilane[6]. This strategy of creating chemical gradients was used on different types of surfaces in the following years. Liedberg and coworkers improvised this strategy to create more restricted and efficient surface energy gradients by interdiffusion methods. Their strategy involves the placement of two different thiol species on opposite sides of a gold substrate. Jan Genzer's group presented several variations of vapor diffusion-based methods for the formation of gradients on surfaces and they used these surfaces as templates for the

controlled assembly of materials and for the controlled movement of droplets. Nicholas Spencer's group developed simple methods for the formation of surface chemical and morphological gradients using controlled slow immersion of substrates into solutions. Ultraviolet ozonolysis (UVO) and similar techniques were used for the oxidation of chemical species present on the surface, allowing the possibility of patterning with shadow masks. Devices like flow coaters were used for creating thickness gradients on soft matter surfaces, presenting a profile of wettability. Gradual adsorption of polymers, gradual polymerization of monomers, simultaneous physical deposition of multiple materials onto the same substrates, and writing of a non-homogeneous solution of immiscible liquids followed by coating are some of the other significant methods used for the creation of gradients.

Research and technology related to gradient surfaces have seen tremendous growth from the time of their creation. A lot of systematic studies have been developed based on gradient surfaces and their possibilities in the field of smart and responsive materials. Through the formation of surface gradients, we can adjust the physicochemical responses of surface and explore its applications. Gradients have variety of applications in the field of smart windows, tissue culture, and microfluidics. The preparation of gradient surface possesses an important role in the field of material science. A variety of physical, chemical and physicochemical strategies were demonstrated for the fabrication of concentration profiles and morphological gradients on soft surfaces, which are based on plasma and UVO methods. Currently existing methods for the creation of gradients on soft surfaces are limited in certain aspects such as the spatiotemporal stability of the gradients, robustness of the gradients, homogeneity of the patterns, and the expensive and sophisticated instrumental requirements. In this context, methods which offer technical simplicity, operational consistency, scalability and spatiotemporal stability of the gradient surfaces are still desired. In this thesis we present our studies on the development of easy, economical, and scalable methods for the preparation of robust gradients on soft surfaces and their applications.

## 2. Review of Literature

Gradient in the context of surfaces means physical or chemical quantity that change from one point to another on a surface. For the last fifteen years, researchers have been trying to create surface gradients, for example concentration gradients, temperature gradients, pressure gradients, etc. from new and efficient methods. In the beginning of nineteen forties, a new

concept regarding gradients was developed and an instrument which measures the melting point of substance was invented, which works based on the concept of gradients[7]. In nineteen seventies Hanak and co-workers published a paper based on the use of gradients. They utilized double-source deposition methods to develop inorganic specimens with a gradual variation in properties along the surface [8]. In nineteen nineties researchers used concept of gradients in developing drugs, and in human genome project [9]. In the subsequent years, concept of gradients became a powerful tool for various inventions, especially in the area of soft materials. Creation of gradient libraries make the fabrication of gradients much easier, as they contains all possible gradient fabrication routes and its taxonomic classification. These fabrication routes can be categorized based on three different methods used: (i) controlling a natural process like diffusion, heat flow, etc. (ii) controlling a gradual process, and (iii) direct deposition methods like laser ablation, sputtering, chemical vapor deposition, etc.

The pioneering work in the fabrication of wettability gradients on surfaces was reported by Chaudhury and Whitesides, using vapor diffusion and distance-dependent exposure of a polished Si wafer to vapors of decyltrichlorosilane [10]. In their work, the regions of the wafer which was near the source becomes more hydrophobic due to the increased exposure to vapors of decyltrichlorosilane, compared to the regions which were away from the source. Due to the wettability gradients produced, a water droplet placed on the gradient surface moved against the gravity. Liedberg and his co-workers created controlled surface energy gradients by the interdiffusion of two different thiols kept at opposite sides of a gold substrate[11]. They introduced a multiple source method for the creation of surface gradients. The resulting surface contains 100% of one thiol species in one side and 100% of other thiol species in opposite side and a mixture of these two in the middle. Jan Genzer's group presented several variations of vapor diffusion-based methods for the formation of gradients on surfaces. They created two dimensional in-plane variation of gradient forming molecules by utilizing mechanically-assembled monolayer (MAMs) on substrates in combination with in-plane symmetric stretching of elastomeric substrates uniformly coated with organosilane precursors and they used these surfaces as templates for the controlled assembly of materials and for controlled movement of droplets [12], [13].

Fisher group developed evaporation based methods for the creation of molecular gradients on flat surfaces and they used surface-sensitive combinatorial near-edge X-ray absorption fine structure (combi-NEXAFS) spectroscopy to characterize the prepared gradients [14].

Spencer's group used a controlled slow immersion technique to create surface gradients on soft surfaces and in this method the deposition of materials on the substrate depends on the speed of immersion and withdrawal of the substrate from the solution [15]. This dip-coating method was an innovative method for the formation of gradients which can be controlled by changing the concentration, pH and ionic concentration of the solution. Various methods for developing gradient libraries and micropatterns with the controlled variations in temperature, substrate free energy, composition, thickness and exposure time are reported in the literature[16]–[19]. Ultraviolet ozonolysis (UVO), plasma treatments and similar techniques were also reported for the controlled oxidation of chemical species and subsequent formation of gradient surfaces[20], [21]. In the ultraviolet ozonolysis method atomic oxygen was used as a strong oxidizing agent for the oxidation of surface species whereas in radio frequency plasma method highly ionized gas plays the role of an oxidizing agent.

Christopher's team introduced the flow coater method to prepare continuous gradient libraries by varying factors like device geometry, motion and concentration of the polymer solution[22]. Thickness is an essential factor in creating gradients in thin polymer films. Various groups used flow coater method for studying the effect of polymer film thickness on phenomena such as wetting of the surface and crazing. Techniques like surface-initiated co-polymerization and gradual polymerization of monomers on silica substrates are also used for the creation of gradients on surfaces[23], [24].

Significant research has been done on the formation of surface wrinkles and gradients on soft surfaces, as this opens up a wide range of applications in the field of materials science. Fabrication of nano and micro structured wrinkles on gradient surfaces enables a wide range of applications such as controlling light's optical properties, cell adhesion, triboelectric, wettability, water collection etc [25]–[30]. Yang and his co-workers studied the wrinkle formation, including mechanical stretching/releasing of oxide/PDMS bilayers and swelling of hydrogel films confined on a rigid substrate with a depth-wise modulus gradient[31]. Alheshibri and Sommers reported a novel technique for moving water droplets on a hydrophilic surface containing a hydrophobic copper background by creating wedge-shaped gradients[32]. Vacuum-based strategy for the fabrication of surfaces with gradient nanoroughness and wettability was introduced by Martin Petr[33]. Ella's group successfully applied surface-initiated copper mediated controlled radical polymerization to prepare poly[(oligoethylene glycol)methyl ether methacrylate] brushes in one pot and developed grafting density

gradient[34]. Continuous and periodic chemical gradients were introduced by Karla Perez-Toralla and Abhiteja Konda using multiple sources of decyltrichlorosilane within custom reaction chambers [35]. Shu Yang and his co-workers studied the mechanism of formation and transition of wrinkle patterns on the surface of soft materials and it was successfully applied to tunable adhesion, wetting and microfluidics[31]. A simple and cost effective strategy for creating mechanoresponsive surface wrinkles using various skin layer elastomeric materials was reported by Jiang's group[36]. Crack-free wrinkles on soft skin elastomeric substrates that can withstand high strain and analysis of their wavelength, amplitude and orientation was reported by Dongjoon Rhee and Won-Kyu Lee[37]. The formation of surface wrinkles on these soft and hard skin elastomeric substrates has significant differences. These crack free wrinkles provide a way for the directional movement of water on soft surfaces. Even though research groups reported several methods for the fabrication of robust surface patterns on PDMS surface, creation of wrinkled morphology on curved surface remains as a challenge. This limitation was overcome by Wang's group by developing an ultrasonic-assisted deposition method to achieve a labyrinth wrinkle pattern above PDMS fiber coated with carbon nanotube [38]. Du and his co-workers developed a high-sensitivity, fast and flexible piezoresistive sensor by placing two layers of silver nanowires (AgNWs) coated polydimethylsiloxane (PDMS) in a wrinkled structure and this shows very low pressure detection time [39]. Recently Tan's group reported the generation of structural color from wrinkled polydimethylsiloxane (PDMS) surfaces, fabricated by plasma exposure and they examined the color tunability and mechanochromic response by adjusting plasma and strain parameters, and by dynamically varying strain [40].

Going through the literature, we were able to observe that the currently existing methods for the preparation of gradients and surface wrinkles were based on expensive methods and sophisticated instrumentation. So, there is a need for simple and inexpensive methods for fabricating surface wrinkles and gradients on soft surfaces.

## 3. Problem identification and objectives

Currently existing techniques for the formation of wettability gradients on soft surfaces rely on sophisticated instrumentation, complex experimental set ups and expensive chemicals. Herein we propose strategies based on modulated crosslinking, which can subdue the drawbacks of currently existing methods. The proposed project aims to develop technically simple general

methods for the fabrication of chemical and morphological gradients on soft surfaces capable of facilitating robust wettability gradients.

- To develop technically simple and novel methods for the fabrication of chemical and morphological gradients on soft surfaces.
- To develop experimental strategies based on differential thermal curing for gradient of softness and morphological gradients.
- To develop experimental strategies based on differential curing through selective deposition of curing agent.
- To characterize the surface gradients through various surface analytical techniques.
- To explore the applications of soft surface gradients.

# 4. Research work carried out

In our research work we have developed three novel experimental strategies based on thermally modulated crosslinking of an elastomeric material for the creation of wettability gradients: (i) Differential thermal curing for gradient of softness, (ii) Differential thermal curing for morphological gradients, and (iii) Selective chemical inhibition of curing.

### 4.1 Work – 1

**Compositionally homogeneous soft wrinkles on elastomeric substrates: Novel fabrication method, water collection from fog, and triboelectric charge generation**

Morphology of soft materials, including those of natural systems has great influence in controlling the functionality and properties of such materials. Responses of soft surfaces to external stimuli and extraneous systems are also directed by structural features of the surfaces. Natural surfaces have purpose-driven and meticulously designed morphological features suitable for specific functionalities. Artificial systems capable of emulating the morphology-dependent physicochemical responses of natural soft surfaces can be prepared through various methods. Wrinkling is an important morphological irregularity on soft surfaces which can be leveraged in this direction. Tunable and responsive nature of wrinkles on natural and artificial soft surfaces makes them an adequate tool for numerous applications in optics, adhesives, stretchable electronics, etc. The formation of soft surface wrinkles created through currently existing techniques rely on expensive chemicals, sophisticated instrumentation and complex

experimental set up. Furthermore, the wrinkles produced through existing techniques are limited in terms of uniformity, tunability and stability. Here, we present a generic and simple spin coating-based method for the formation of surface wrinkle on elastomeric substrates making use of buckling instability in a bilayer system with different elasticities in each layer. A model elastomeric material, polydimethylsiloxane (PDMS ) was used for demonstrating this strategy. An uncured PDMS film of different elastomer-curing agent ratio was spin coated onto a mechanically stretched PDMS film with definite elastomer-curing agent ratio. Thermal curing followed by the release of pre-strain leads to the formation of wrinkles **(Figure 1).**

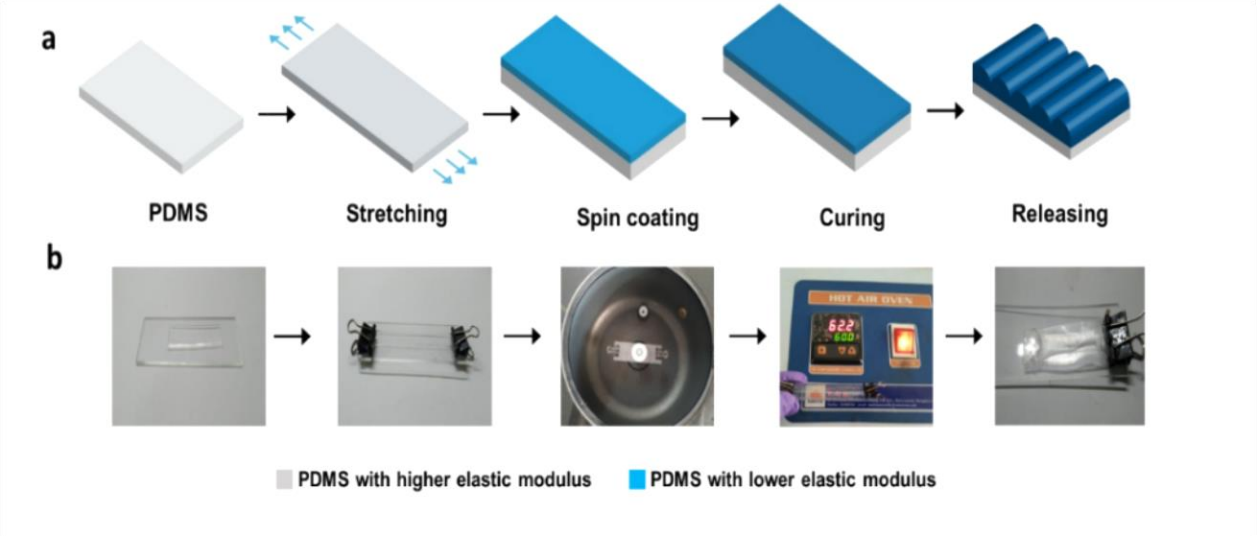


**Figure 1.** Schematic illustration and (b) Digital photographs representing different steps in the process of preparing wrinkles on PDMS bilayer films.

To study the effects of spin coating speed (resulting in a change in thickness of the top layer) and amount of applied pre-strain on wrinkle parameters experimentally, we chose three different spin coating speeds (600 rpm, 900 rpm, 1200 rpm ) and pre-strain values ( 50 %, 65 %, 85 % ). Tunability of wrinkle dimensions is critical as it has an important role in practical applications of the soft wrinkles. We tried to develop wrinkles of different dimensions on PDMS bilayer films by varying spin-coating speed and applied mechanical pre-strain. Optical microscopic and profilometric images of the wrinkled samples (**Figure 2, 3**) showed that the number of wrinkles formed per unit length increases with an increase in pre-strain values and spin-coating speed.

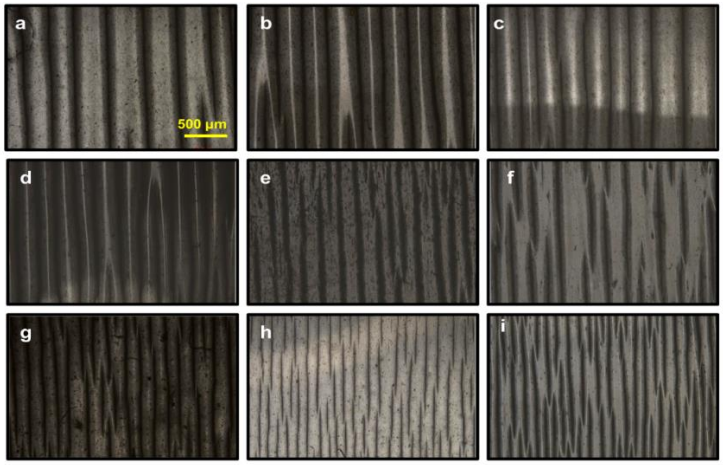


**Figure 2**. Optical microscopic images of wrinkled PDMS films prepared using different conditions. (a) 50 %, (b) 65 %, and (c) 85 % pre-strain spin coated at 600 rpm; (d) 50 %, (e) 65 %, and (f) 85 % pre-strain spin coated at 900 rpm; (g) 50 %, (h) 65 %, and (i) 85 % pre-strain spin coated at 1200 rpm (Scale bar = 500 µm, applicable for all the images).

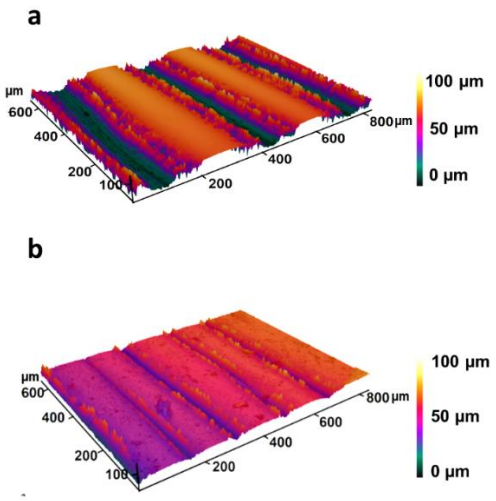


**Figure 3.** Representative optical profilometer images from the wrinkled PDMS surfaces. (a) 50 % pre-strain spin coated at 900 rpm, (b) 50 % pre-strain spin coated at 1200 rpm.

The wrinkled PDMS substrates prepared exhibited modulation of transmittance and diffraction properties in response to mechanical deformations as shown in **Figure 4**. The uniformity and hydrophobic nature of wrinkled PDMS surfaces show efficient water collection, providing an alternate solution for the scarcity of pure drinking water, especially for arid and desert regions (**Figure 5**). Also the wrinkled substrate exhibit an enhanced triboelectric charge generation compared to plain PDMS as shown in **Figure 6**.

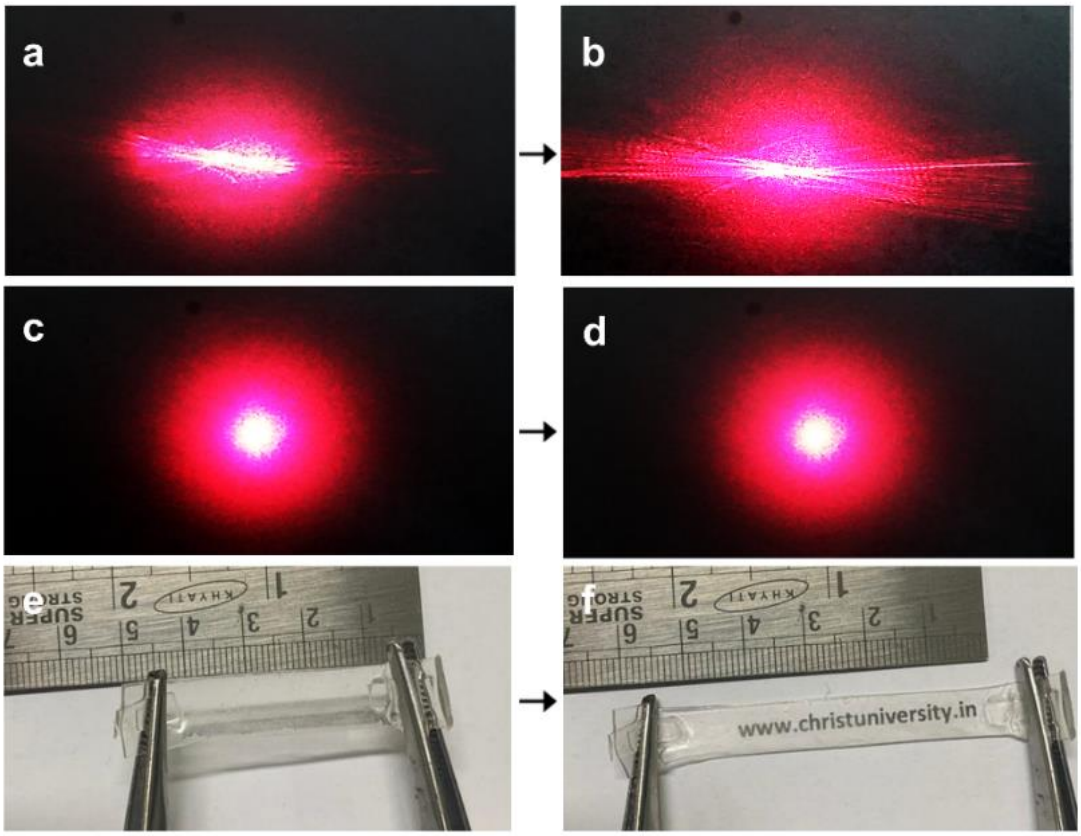


**Figure 4**. Digital photographs of wrinkled PDMS (a) unstretched (b) stretched and plain PDMS (c) unstretched (d) stretched exhibiting change in diffraction properties and wrinkled PDMS (e) unstretched (f) stretched exhibiting reversible optical properties.

**Figure 5.** Schematic of water collection set up

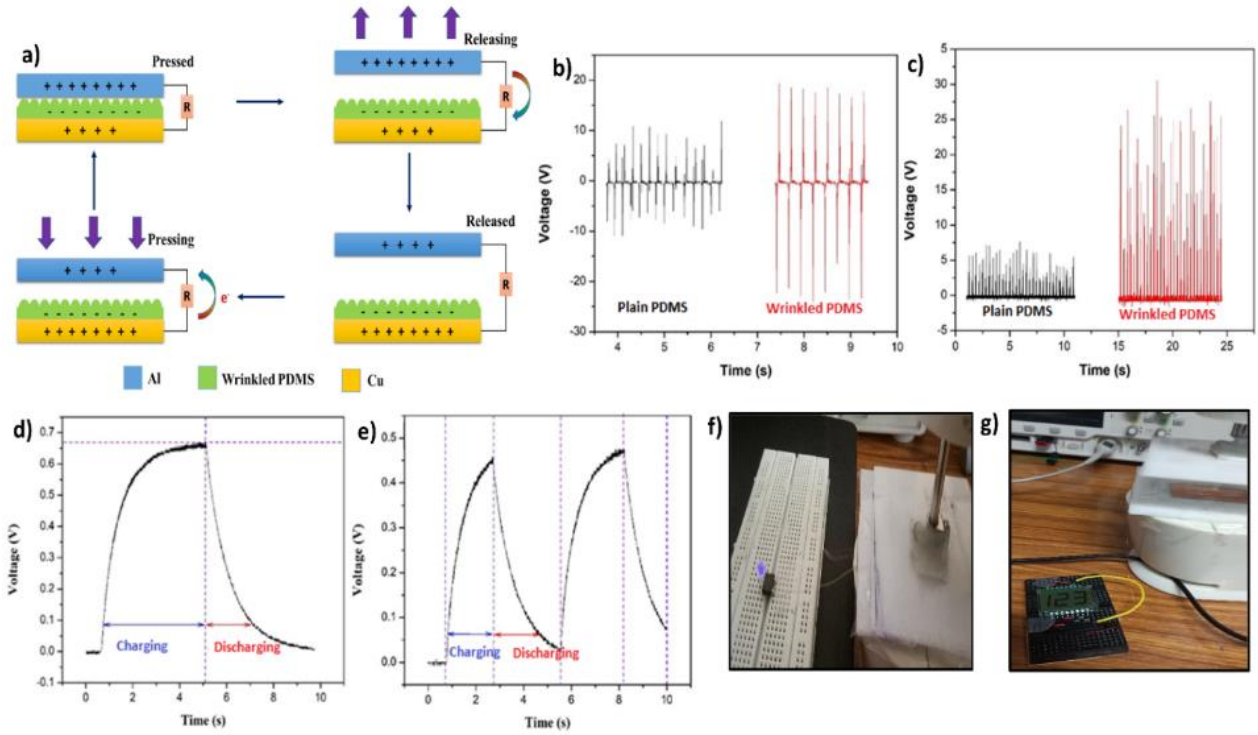


**Figure 6.** (a) Working mechanism of contact and separation mode TENG. (b) Voltage response of plain PDMS TENG and wrinkled PDMS-TENG, (c) Rectified Voltage response of plain PDMS TENG and wrinkled PDMS TENG. (d) Charging and discharging of 0.1 µF capacitor, (e) Charging and discharging cyclic characteristics of wrinkled PDMS TENG with 0.01µF capacitor. (f) Glowing LED using wrinkled PDMS TENG, (g) Powering up LCD display (Shows 123) using wrinkled PDMS TENG.

### 4.2 Work – 2

**Robust wettability gradients on soft surfaces through differential thermal curing of elastomers**

This work presents a novel method for the creation of wettability gradients on soft surfaces. Differential thermal curing was used as an operational tool for the preparation of gradients. We have used two different routes to get the differential thermal treatment of the soft substrate. In the first method, we prepared a PDMS film of elastomer crosslinking ratio 15:1 and it is half cured by placing in an oven. During a second stage of curing, half of the substrate was fixed on a hot surface and the remaining was exposed to a cold surface (may be air, metal or wood). This leads to the differential thermal curing of PDMS film. At a given elastomer-crosslinking agent ratio, crosslinking of the PDMS depends on the temperature. The differential heating applied through this experimental set up thus create a gradient of crosslinking across the PDMS film. Extend of crosslinking in PDMS is directly proportional to its elastic modulus and hardness. Hardness of the surface in turn is directly related to hydrophobicity, which will

apparently facilitate the gradient of wettability on PDMS surface. Contact angle measurements confirmed the formation of gradient on PDMS film.

In the second method, we used slanted surface upon which the curing of PDMS was carried out. Partially cured PDMS films (15:1) were kept over a slanted and thermally conducting surface (which is a metal piece or some 3D printed shapes), placed on a heat source in such a way that different points on the film are at different separations from the heat source as shown in **Figure 7** . Depending on the separation of each point from the heat source, different amount of thermal energy will be supplied to the film at that point. At a given elastomer-crosslinking agent ratio, crosslinking of the PDMS depends on the temperature. The differential heating applied through this experimental set up will thus create a gradient of crosslinking across the PDMS film. Extend of crosslinking in PDMS is directly proportional to its elastic modulus and hardness. Hardness of the surface in turn is directly related to hydrophobicity, which will apparently facilitate the gradient of wettability on PDMS surface. Contact angle measurements confirmed the presence of gradients (**Figure 8**). Wettability gradient prepared on PDMS surface deteriorated within one week of storage in ambient conditions. We can increase the stability and shelf-life of the samples by storing them at lower temperature. Also, we developed a benzophenone treatment method to enhance the stability of these wettability gradients at room temperature (**Figure 9**). We conducted cell adhesion studies on the surfaces which further confirms the presence of the gradient behavior. Cell adhesion was enhanced in the hydrophobic area compared to that in hydrophilic area (**Figure 10**). Also, directional water collection from was observed for these gradient samples.

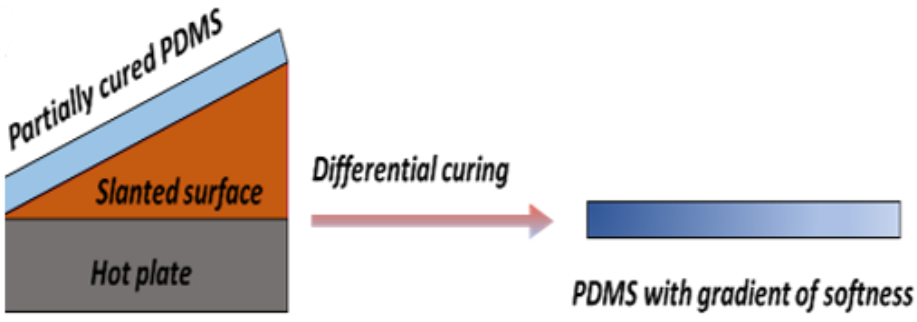


**Figure 7**. Schematic representation of differential thermal curing for gradient of softness.

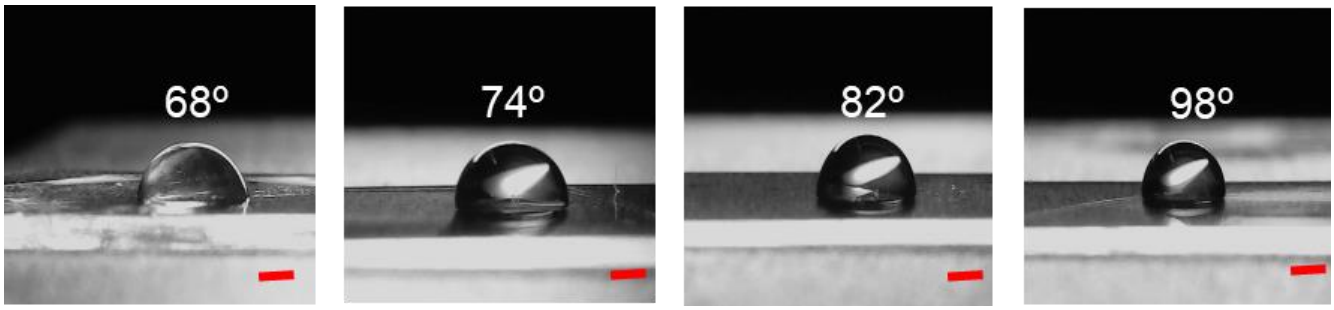


**Figure 8**. Contact angle measurements from different locations of the gradient surface (Scale bar = 50 µm)

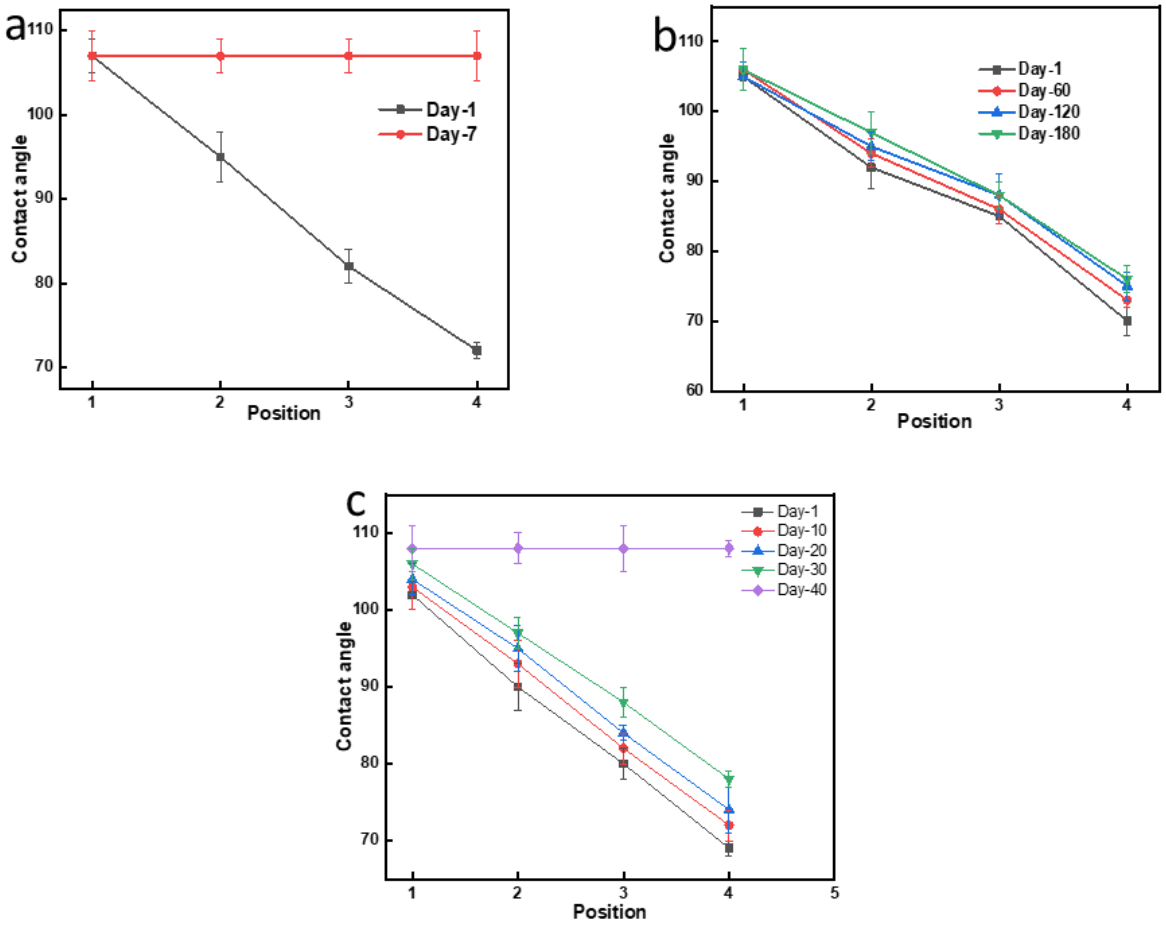


**Figure 9.** Contact angle measurements of samples kept at (a) room temperature, (b) lower temperature, (c) treated with benzophenone.

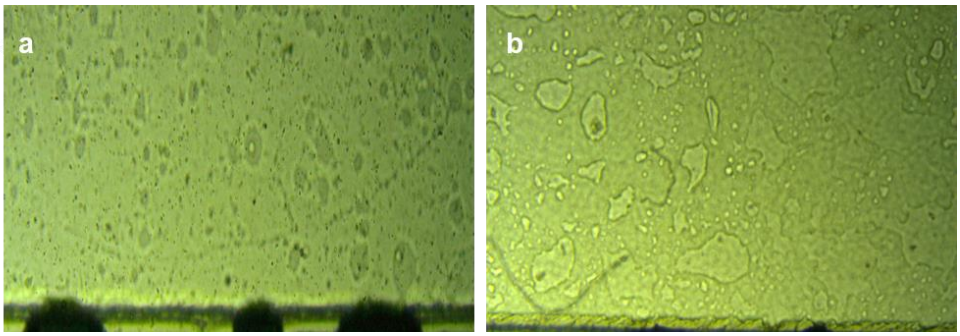


**Figure 10.** Cell adhesion studies above prepared samples(a) hydrophilic end (b) hydrophobic end (Magnification = 40x)

### 4.3 Work – 3

**Fabrication of morphological gradients on soft surfaces and its applications.**

In this work, we are presenting a novel strategy for the preparation of morphological gradients on soft surfaces. In this method we are placing a PDMS bilayer system on a slanted surface which was kept over a hot surface for curing as shown in **Figure 11**. This causes crosslinking in the top layer of the bilayer system. Crosslinking across the top layer won't be spatially identical because the thermal energy available at different locations are not the same. This results in the formation of a PDMS layer with decreasing hardness across the film. After the curing, the strain in the bilayer system is released, which results in buckling instability induced wrinkling. Wrinkle formation is inferred to emerge from the difference in elastic modulus of the top and bottom layers. Areas where there is a larger difference in the elastic moduli will wrinkle more and the amplitude of wrinkles will be higher in those regions.

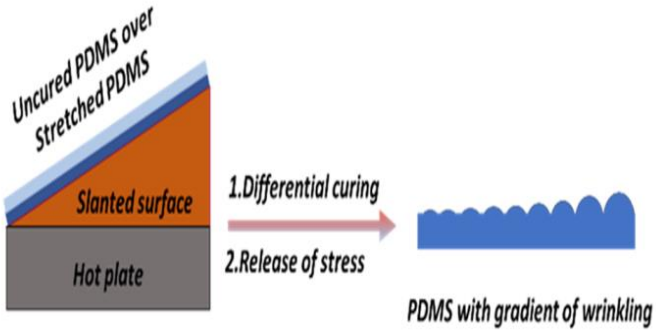


**Figure 11.** Schematic representation of differential thermal curing for morphological gradients.

Areas with lesser difference of elastic moduli between the top and bottom layer of the film will form wrinkles with lower amplitude. This contrast in the extend of wrinkling results in the formation of morphological gradient across the resultant PDMS film. The morphological gradient thus fabricated shows a gradient of wettability which is confirmed using contact angle measurements (**Figure 12**) and mechanoresponsive optical properties. Gradient surface prepared exhibit directional water collection as shown in **Figure 13**. Also it shows controlled triboelectric charge generation (**Figure 14**).

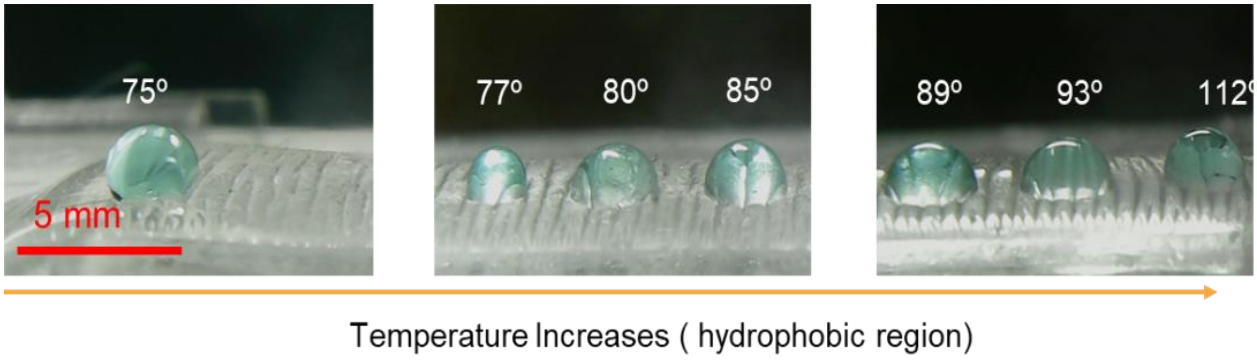


**Figure 12.** Contact angle measurements of droplets at different locations above morphological gradient surface.

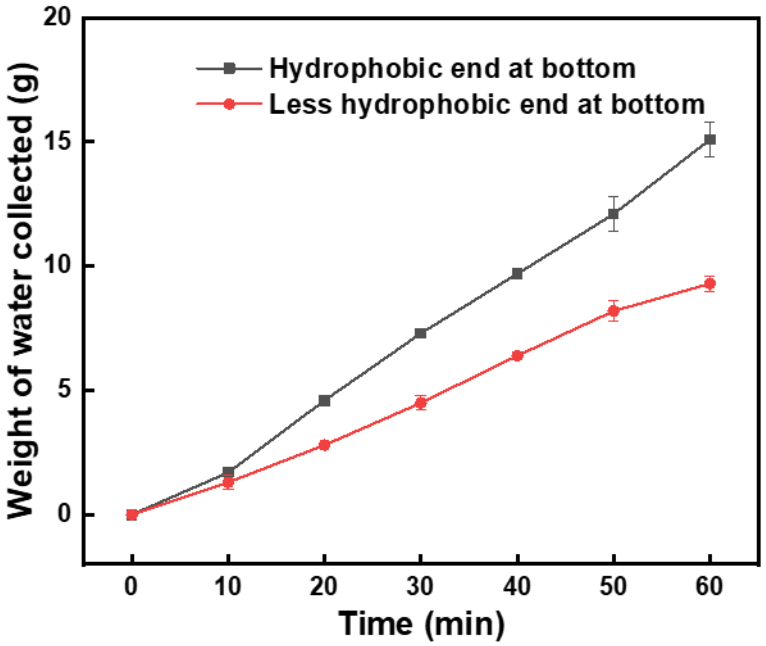


**Figure 13.** Directional water collection from fog using the prepared gradient sample.

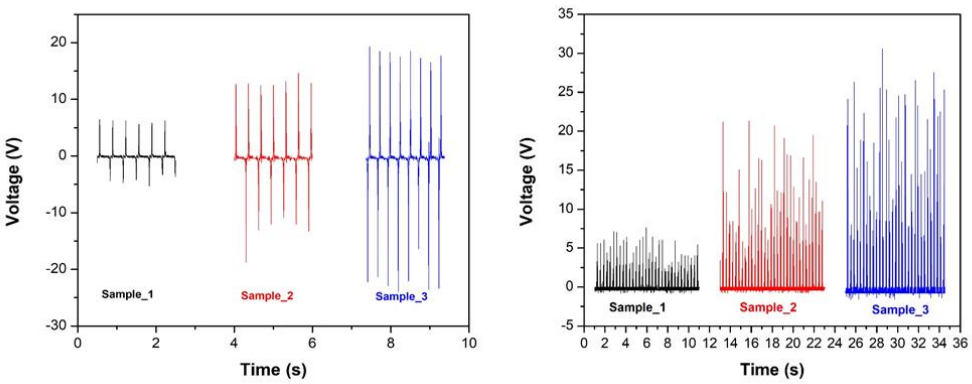


**Figure 14.** Voltage and rectified voltage response at different locations of morphological gradient surface.

### 4.4 WORK -4

**Robust wettability gradients on soft surfaces through patterned chemical inhibition of curing.**

Herein we present a strategy prepare wettability gradients on soft surfaces using modulated exposure of the surface to a UV source. Benzophenone is used as a chemical inhibitor against normal curing process. During the normal curing process of PDMS, hydrosilation of olefins takes place and the resulting product is completely cured and insoluble. But, in the presence of benzophenone, stable radicals and short complexes were formed which inhibit the normal curing process. A partially cured PDMS film was synthesized by mixing elastomer curing agent ratio 15:1, benzophenone and xylene in 3:5 ratio. Then the above sample was placed above a slanted surface which is kept under a UV source (**Figure 15**). The site-specific graduated exposure of benzophenone under UV light inhibits curing and leads to the formation of stable radicals. After that the PDMS sample was cured for 2 hours in hot oven. Contact angle measurements confirmed the presence of wettability gradients (**Figure 16**). The stability of the prepared samples was more compared to samples prepared by differential thermal curing. The prepared sample also exhibit directional water collection (**Figure 17**).

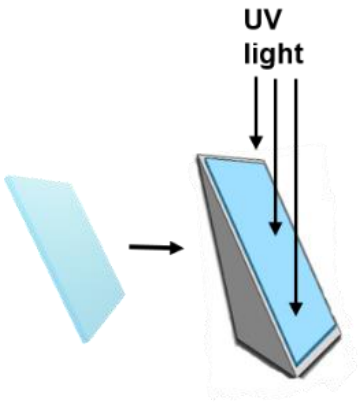


**Figure 15.** Schematic representation of patterned chemical inhibition of curing

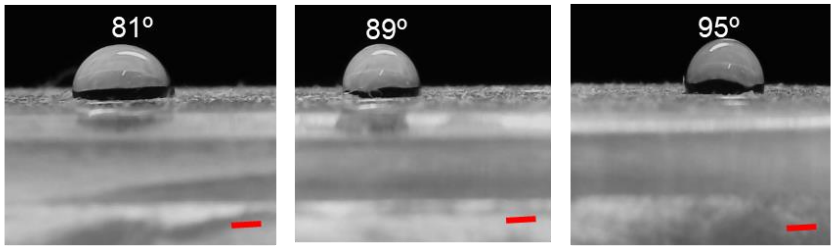


**Figure 16.** Contact angle measurements of droplets at different locations above the gradient surface.

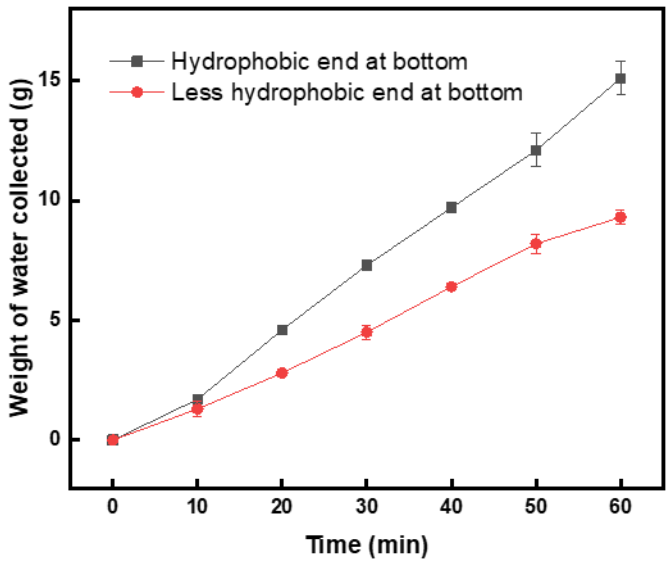


**Figure 17.** Directional water collection from fog using the prepared gradient sample.

## 5. CONCLUSION

Periodic features in the surface morphologies of natural and artificial soft materials are known to effectuate morphology-driven and stimuli-responsive functionality through switchable or tunable adhesion, wettability, and optical responses. Easy and robust methods to prepare morphological and chemical gradients on soft surface with controlled structural features are required for customizing and optimizing the application of soft materials in various technological disciplines. Addressing this scope, we demonstrated four generic and simple methods for the fabrication of gradients on soft surface of polydimethylsiloxane (PDMS). PDMS was chosen as a model elastomer because of its attaractuve properties pertinent to various applications. The methods we demonstrated can be extended to other elastomers of comparable properties.

Making use of buckling instability we fabricated soft surface wrinkles on polydimethylsiloxane (PDMS) bilayer system with different elasticities in each layer. PDMS with lower elastic modulus was spin-coated onto a mechanically stretched film of PDMS with a higher elastic modulus. Thermal curing followed by the release of pre-strain resulted in the formation of wrinkles in the top layer of the PDMS. The structural features and the hydrophobic nature of the wrinkled PDMS surfaces enabled us to demonstrate efficient water collection from fog using these substrates. The soft surface wrinkles exhibited triboelectric charge generation and triboelectric nanogenerator (TENG) devices were prepared using the substrates. Furthermore, the substrates showed high mechanical stability and mechanoresponsive optical behaviours.

We fabricated hierarchical wrinkles on soft surfaces by differential thermal curing of homogenous PDMS bilayer systems. These morphological gradients thus fabricated shows a gradient of wettability which is confirmed using contact angle measurements and mechanoresponsive optical properties. They also exhibit enhanced water collection from fog and triboelectric charge generation. The simplicity and general applicability of these methods we present here is expected to establish promising pathways towards the formation of soft wrinkles in other elastomeric systems also with important applications in various fields.

In another part of our work, we fabricated robust wettability gradients on soft surfaces through differential thermal curing and selective chemical inhibition of curing of partially cured elastomers. Contact angle measurements confirmed the formation of gradient on PDMS film.

Cell adhesion studies and directional fog collection of the prepared gradients were also established.

The thesis will be comprised of seven chapters. Chapter 1 and 2 will be presenting introduction and literature review on morphological and chemical gradients on soft surfaces. Chapter 3 will explain the fabrication of robust and tunable soft surface wrinkles with mechanoresponsive optical properties, water collection from fog and triboelectric charge generation. Chapter 4 will elucidate the fabrication of robust wettability gradients on soft surfaces through differential thermal curing of elastomers. Fabrication of morphological gradients on soft surfaces through differential thermal curing will be explained in Chapter 5. Chapter 6 will discuss the creation of wettability gradients through selective chemical inhibition of curing. Chapter 7 will present the conclusions of whole research work and will be followed by publications and conference proceeding details.

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2. **Soorya S Raj** and Vinod T. P. - Poster presentation on paper entitled " A generic method for the fabrication of soft surface wrinkles for efficient fog collection" in International e-conference on physics of nanomaterial and nanotechnology (ICPN-2021) held at Mangalore University during October 28-30, 2021.

3. **Soorya S Raj** and Vinod T. P. - Oral presentation on paper entitled "Facile spin-coating based method for the fabrication of mechanoresponsive soft surface wrinkles" in indo-South Korea International e-Conference on "Nanoscience and Nanotechnology for Energy, Environment and Biomedical Applications" (iNEEBA2021), organized by Vinayaka Missions Kirupananda Variyar Arts and Science College, India in association with Gyeongsang National University, Republic of Korea during 07- 08 October, 2021.

**Manuscript under preparation**

1. **Soorya S Raj** and Vinod T. P., Bio-inspired robust wettability gradients on soft surfaces through differential thermal curing of elastomers.

2. **Soorya S Raj** and Vinod T. P, Fabrication of morphological gradients on soft surfaces through differential thermal curing of elastomers.

3. **Soorya S Raj** and Vinod T. P, Robust wettability gradients on soft surfaces through patterned chemical inhibition of curing.